Chapter 4

Optimised Cement Design

OPTIMISED CEMENT DESIGN

1. INTRODUCTION

The process of cement design consists of the following interrelated steps:

1) selection of the most convenient set of components
2) determination of the relative proportions of the components
3) definition of the fineness and grain size distribution of cement (compound grinding) or the cement components (separate grinding)

The objective of the cement design is to achieve the specified or desired performance of the cement at the minimum possible cost.

The procedures applied in practice for cement design are usually based on analytical tools (models to predict cement performance), experiments (trials on laboratory and industrial scale) and on experience. The better the knowledge of the relationships between cement components, proportioning and processing and the cement properties, the easier it is to arrive at the optimum solution.

The optimisation of the cement design requires nowadays more attention than in earlier times. The main reasons for this development are:

- increase in number of cement components (use of mineral components and chemical admixtures in the cement)
- use of new grinding technologies (roller press, vertical mill, Horomill) having an effect on the resulting grain size distribution and grinding temperature
- extension of product and application range

The object of the present paper is to describe the basic considerations influencing the cement design and to give an overview on the influence of the cement components, their proportioning and cement grinding on the properties of cement.

2. BASIC CONSIDERATIONS FOR CEMENT DESIGN

2.1 Product requirements

The cement design will strongly depend on the performance requirements to be fulfilled by the cement. These requirements, which are determined by the respective standards and by the market, may comprise specifications on.

- proportioning of cement components and chemical composition
- workability (water demand, setting), volume stability and strength
- special properties:
    - heat of hydration
    - sulphate resistance
    - alkali-aggregate reactivity
    - shrinkage, etc.

Besides the above specifications, there may be further requirements with regard to the handling of the cement (i.e. temperature, flowability and storage stability).

In the future, also certain requirements with respect to energy consumption and emissions (in particular CO2) during the cement production may be imposed.

2.2 Available cement components

The flexibility in cement design will be obviously controlled to a large extent by the available cement components. The most important aspects of the cement components (clinker, mineral components and gypsum) in this respect are:

- available quantities
- quality / uniformity and
- costs

The cement plants usually count with one "normal" type of clinker, whose characteristics are pre-determined by the raw material situation and by the burning and cooling conditions in the kiln. Occasionally, also special clinkers are produced for certain cement types, but with the increased use of mineral components in the cement, which allow to obtain special properties with "normal" clinker, less and less of such clinkers will be applied in the future.

The availability of the mineral components varies from country to country. The main industrial by-products used for cement production - blast furnace slag and fly ashes - are principally available world-wide in great quantities (see Table 1); however, only part of it complies with the necessary quality requirements for an application in the cement. Among the natural mineral components, limestone of suitable quality should be available at all cement plants, whereas the natural pozzolans are less wide-spread.

Table 1: Estimated production of fly ashes and blast furnace slags (Mio t/a)

	Blast furnace slag (1994)	**Fly ash (1992)**
Western Europe	36	61
Eastern Europe (+ former USSR)	28	95
North America	20	51
Latin America	11	3
Africa	3	24
Asia	78	125
Australia	3	7
World	178	366

Natural gypsum deposits are scarce in some countries. In such cases, alternative materials like natural anhydrite and limestone or by-product gypsum from other industries have to be considered.

The different type of chemical admixtures, which can be added at the cement grinding stage, can in principle be purchased anywhere in the world.

2.3 Production facilities

The available production facilities (in particular the cement grinding installations) put certain constraints on the cement design. Such constraints may lead to limitations with respect to:

- clinker factor
- fineness range of cements
- feasible number of products
- type of cement grinding (compound or separate)

Moreover, the cement design will be influenced decisively by the type of cement mill used for grinding. For instance, with the new grinding technologies, adjustments have to be made to account for the differences in grain size distribution and grinding temperature compared to the traditional systems.

2.4 Economy

The production costs of cement basically consist of the costs of the materials entering the cement mill and the grinding costs. From the two factors, the material costs generate by far the greatest part of the production costs.

The most expensive material in the cement is usually the clinker. The minimisation of the clinker content in the cement is therefore the single most important factor in reducing the production cost, provided that mineral components of suitable quality are available at convenient prices.

The principal ways to reduce the clinker factor in the cement are:

- adjustment of the fineness and grain size distribution of the cement and its components
- use of high quality clinker
- use of chemical admixtures already in the cement

The possible clinker reduction is of course limited by the factors discussed in the previous chapters.

3. INFLUENCE OF CEMENT COMPONENTS ON CEMENT PROPERTIES

3.1 General

Due to the great variety of factors involved, it is difficult to describe precisely the relationship between the cement components and the cement properties. The available models for the prediction of cement performance usually only reflect the general trends.

The effects on the cement properties are best understood for the clinker and gypsum. Least knowledge is available in case of the mineral components and the chemical admixtures, so that virtually the only way to assess their influence is to carry out performance tests.

3.2 Clinker

The composition of clinker gives some indications on the properties of cement to be expected, as it influences the rate of hydration reaction and thus the setting and hardening rate of cement The composition of clinkers control the quantity and rate of heat evolved during hydration and the resistance of cement to sulphate attack; therefore, limiting values are specified.

In this section, the influence of composition of clinker on the following properties of cement shall be discussed:

- water requirement of standard paste and consistency of concrete
- stiffening rate and setting time of standard paste and slump loss of concrete
- heat of hydration
- strength of mortar and concrete
- sulphate resistance
- other properties of concrete

A summary on the relationship between clinker composition and the principal cement properties workability (water demand, setting) and strength is given in Table 2.

Table 2: Effect of clinker composition on water requirement and setting time of standard paste and compressive strength of ISO mortar (general trends)

Clinker	Water req.	Setting time	Strength	
			early	final
C3S	--	--	↗	↗
C2S	--	--	↘	↗
C3A	↗	↘	↗	↘
C4AF	--	--	↘	↗
K2O	↗	--	↗	↘
Na2O	↗	--	↗	↘
SO3	--	↗	↗	↘
P2O5	--	↗	↘	--

↗ increasing
↘ decreasing
-- no effect

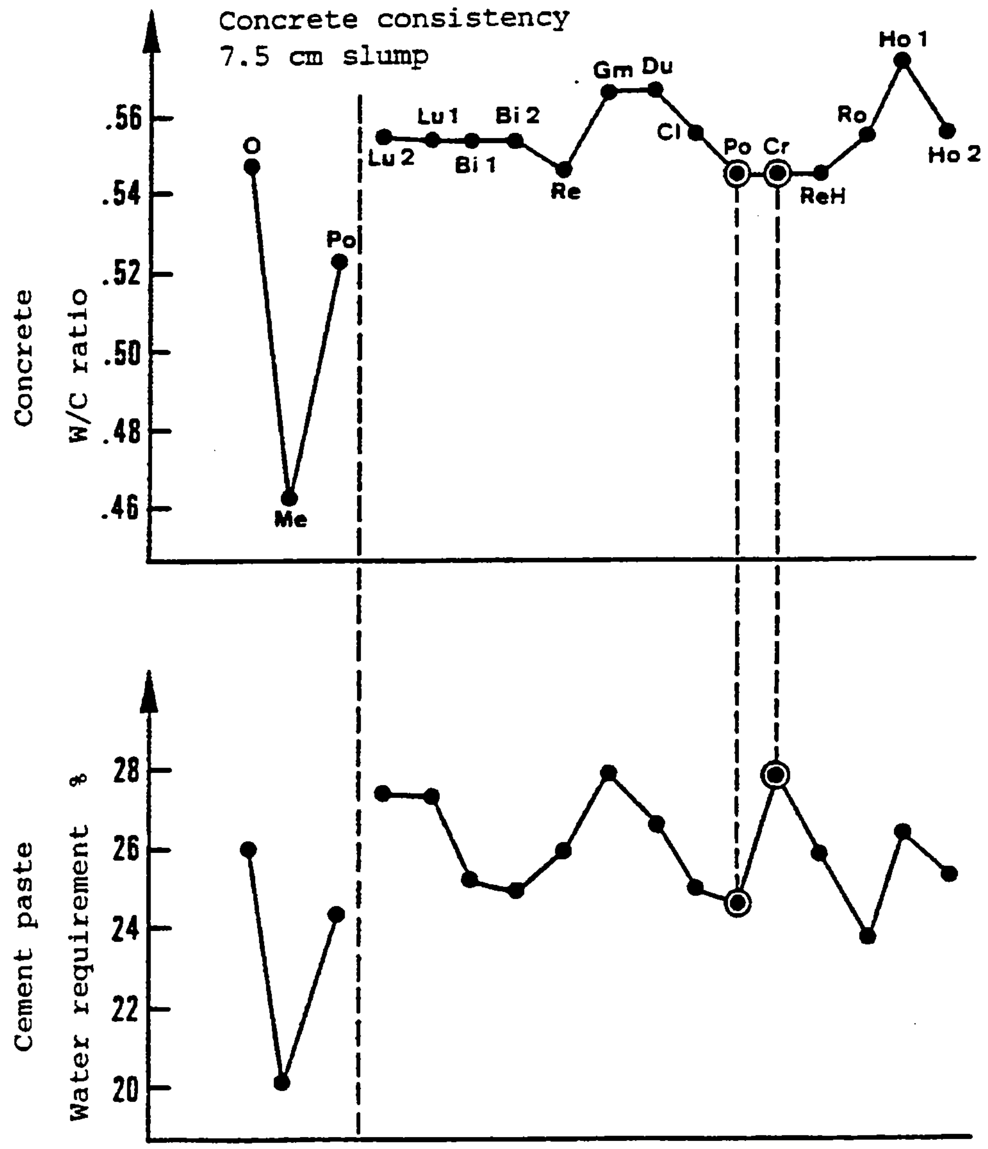
3.2.1 Water requirement of standard paste and consistency of concrete

The water requirement of the standard paste of normal consistency depends primarily on the aluminate and alkali content of clinker and on the fineness of cement. From a multiple regression analysis carried out at HMC on 48 different ordinary Portland cements, the following relation between the water requirement and cement composition was derived:

W.r. % = $17.4 + 0.15\,a + 0.26\,b + 0.12\,c$
a = particle size fraction 10 to 30 µµ in wt %
b = C3A content in wt % (Bogue's formula)
c = total alkali content in wt %

The relation between the water requirement of standard paste and the composition of cement cannot be applied to concrete, as there is a rather weak relationship between the water requirement of paste and water/cement ratio of concrete (see Figure 1)

Figure 1: **Water requirement of cement and w/c-ratio of concrete**



Po	-	Water reducing admixture (Pozzolith)
Me	-	Superplasticizer (Melment)
Lu 2 ... Ho 2	-	various OPC
Gm, Du, etc.	-	various Group plants

The effect of cement on the consistency or water requirement of concrete is rather small compared to other factors, such as sand, admixtures and temperature. An exception is concrete with a very short mixing time, where cement with false set may seriously impair the consistency of concrete.

3.2.2 Rate of stiffening and setting time of standard paste and slump loss of concrete

The stiffening rate or the „Vicat" setting time of the standard paste is significantly influenced by the composition of clinker. The sulphates and phosphates of clinker usually delay, whereas aluminate shorten the setting time of cement.

The relation between the stiffening rate or setting time of standard paste and the stiffening rate - expressed as slump loss - of concrete is, just as for the water requirement, rather poor. Therefore, it is difficult to estimate the stiffening rate of concrete on the basis of composition or fineness of cement.

3.2.3 Heat of hydration

The effect of the clinker composition on heat of hydration has already been discussed in detail in the paper on cement hydration. The principal way to control the heat evolution of the clinker is the adjustment of the C3S and C3A content.

3.2.4 Strength of mortar and concrete

The rate of strength development of mortar or concrete depends on the type (or composition) of cement. The general tendency of cements with a slow rate of hardening is to have a slightly higher ultimate strength.

The ASTM type IV cement, with low content of C3S, has the lowest early strength, but develops the highest ultimate strength (see Figure 2). This agrees with the influence of individual clinker components on the rate of strength development measured on pure clinker minerals (see Figure 3).

Figure 2: Strength development of concrete made with different cement types

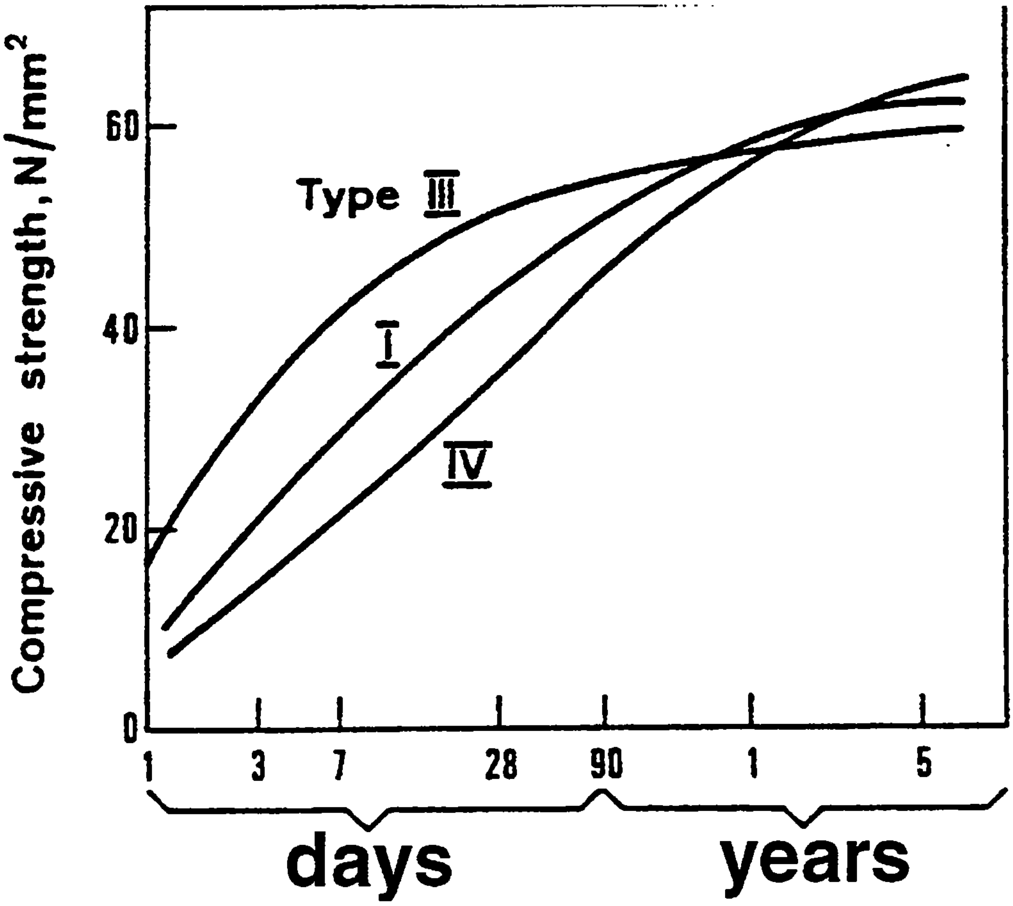
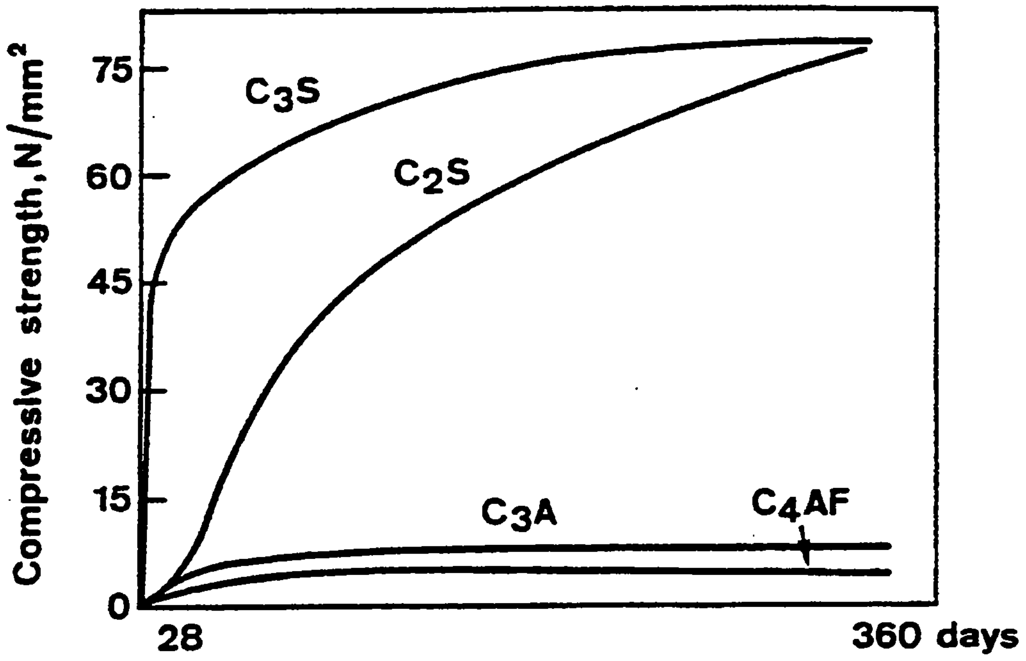


Figure 3: Compressive strength of cement compounds



The two calcium silicates develop the highest strength, but at different rates. The aluminate develops little strength, despite a high rate of hydration.

The rate of strength development of mortar or concrete depends on the clinker composition as follows:

a) **Calcium silicates.** The different rates of hydration of C3S and C2S affect the rate of hardening in a significant manner: A convenient rough rule assumes that C3S contributes the most to the strength development during the first four weeks and C2S afterwards. In general, somewhat higher ultimate strengths are reached by cements with lower calcium content, i.e. rich in C2S. This observation corresponds with the assumption that the strength of cement depends on the specific surface of its hydration products. C2S produces more colloidal CSH gel and less of the crystalline $Ca(OH)_2$ than the C3S.

b) **Aluminates and ferrites.** The influence of the other two major components on the strength development is still controversial. Presumably, the C3A contributes to the strength of the cement paste during a period of one to three days. In general, both aluminate and ferrite contribute to the strength of cement to a minor extent, but significantly influence the hydration process of the silicates and thus have an indirect effect on the rate of hardening.

c) Of the **minor components,** the alkali sulphates exert the greatest influence on the rate of hardening. The alkali sulphate - mostly present as easily soluble potassium sulphate or calcium-potassium sulphate with a molar ratio of 2:1 to 1:2 - accelerates the rate of hardening, improving the early strength and decreasing the 28 day and ultimate strength (see Figure 4). Of the other minor components, fluorine accelerates, whereas the phosphorous compound delays the rate of hardening.

d) **Clinker characteristics other than chemical composition.** Particularly the burning and cooling conditions influence the rate of hardening of a particular clinker composition. Frequently, clinkers of the same chemical composition have different strengths and clinkers of different chemical composition have the same strength. A simple experiment proves that the very same clinker composition may have rates of hardening which vary considerably. Reburning of a clinker in a laboratory furnace changes the rate of hardening, but does not affect the chemical composition of clinker (see Figure 5).

Figure 4: Effect of soluble K2O on the compressive strength of ISO mortar

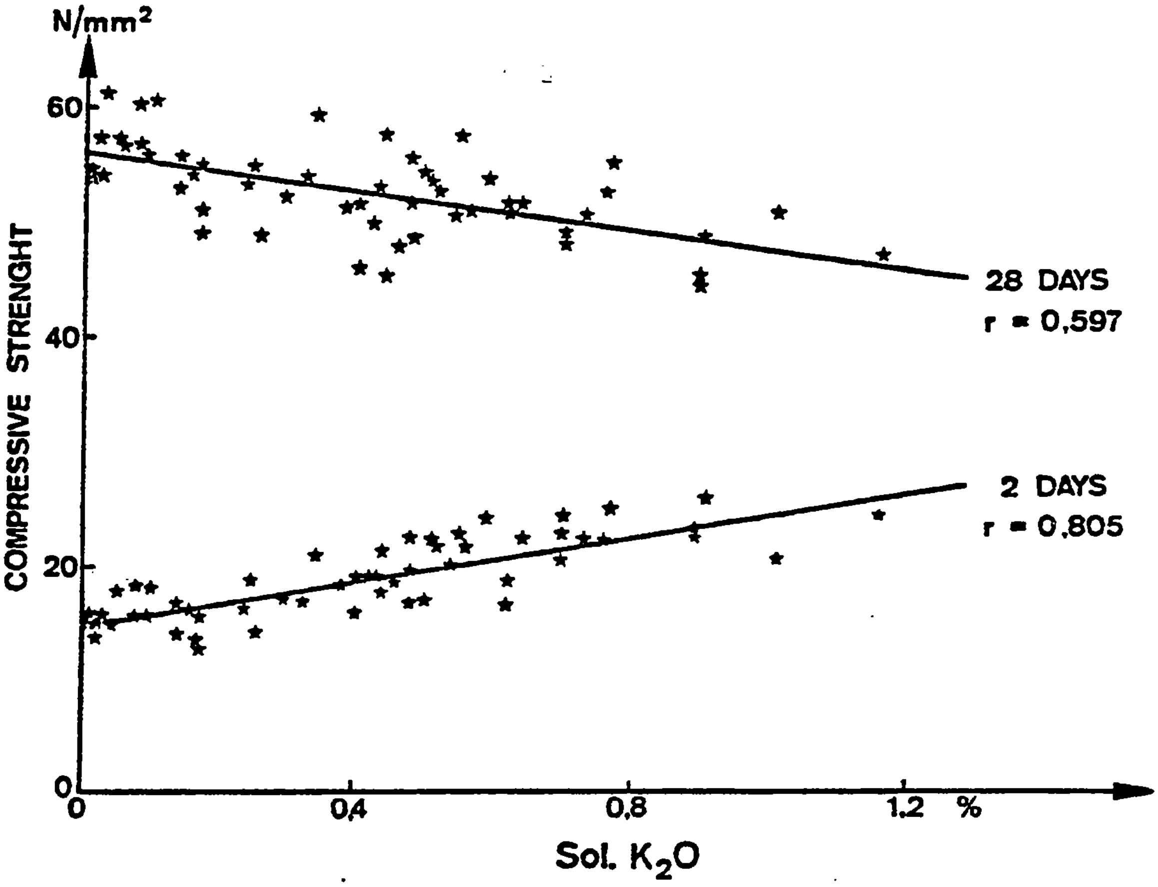
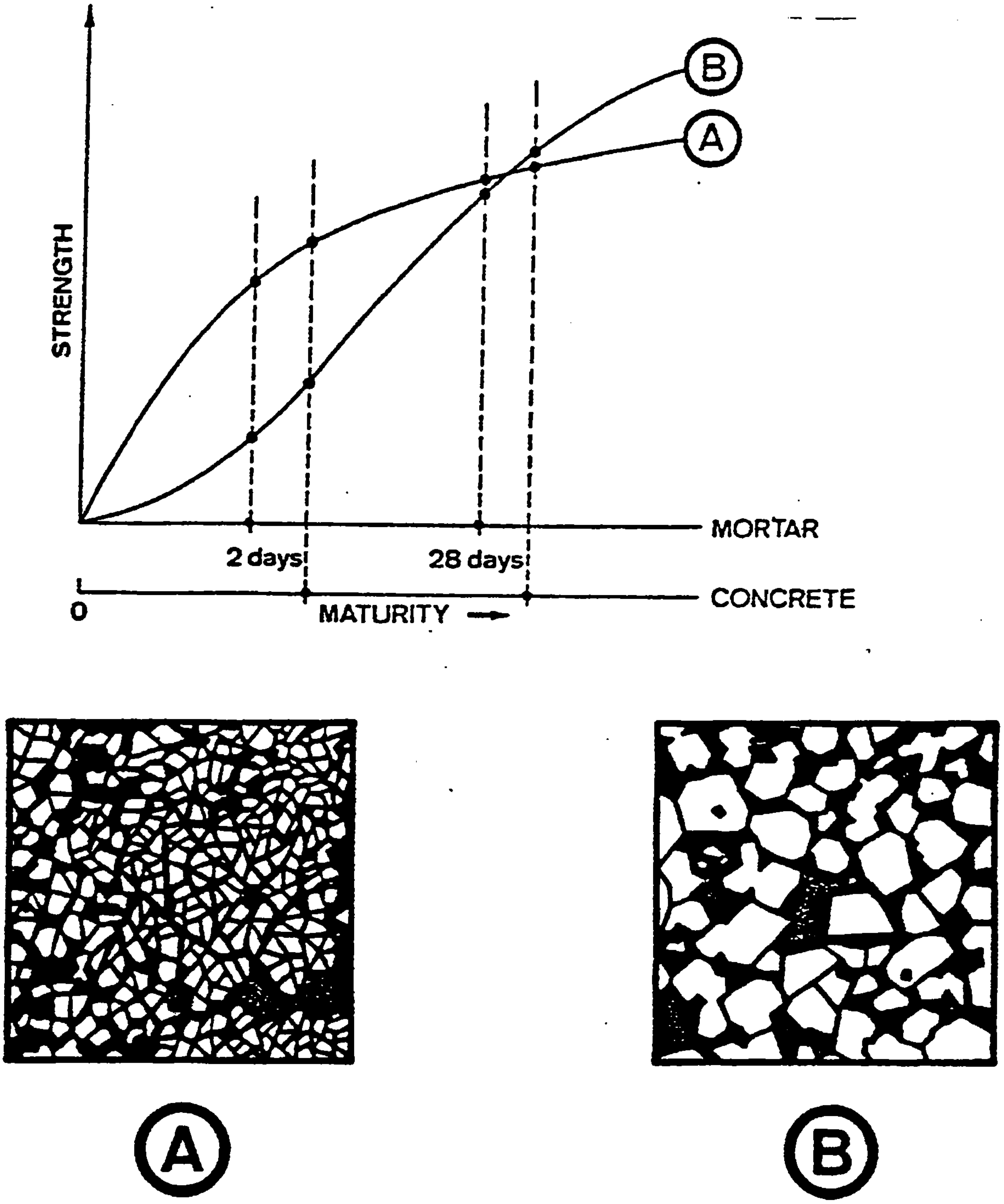


Figure 5: Model of strength development of mortar and concrete made with two clinkers of same chemical composition and different activity



A = Clinker of high activity
B = Clinker of low activity
Maturity ≅ Degree of hydration

A general guide on the necessary amount of the main clinker phases to achieve optimum strength development is given in Table 3. The most essential point is to have a high C3S content (in the order of 60%) and to adjust the C3A content.

Table 3: "Ideal" composition of the clinker for optimum strength development

Clinker phase	"Ideal" content (%)
C3S	55 - 65
C2S	15 - 25
C3A	7 - 10
C4AF	7 - 10

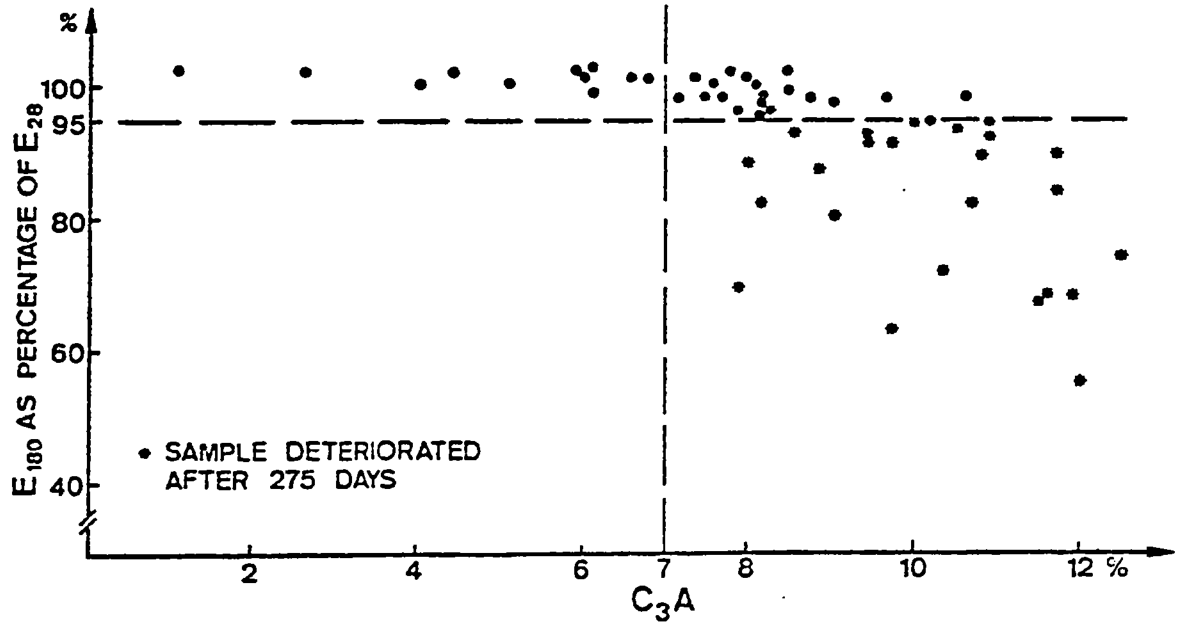
The influence of the clinker composition on the standard mortar strength is noticeably reduced in concrete. Depending on the quality of cement, sand and aggregate, the proportioning of concrete or mortar components, curing temperature, specimen dimension, the rate of hardening in mortar and in various concrete compositions is quite different.

Moreover, the use of admixtures in concrete - which is common practice today - makes the relation even more complicated. Due to different hardening rates of mortar and concrete, the relation between concrete and mortar strength at various ages varies and depends on the above mentioned factors. Concluding, the cement properties, as demonstrated through standardised testing methods, do not show their effect in the same way in concrete.

3.2.5 Sulphate resistance

The sulphate resistance of concrete depends primarily on the C3A content of clinker. The ferrite phases (C4AF) affect the sulphate resistance to a much lesser degree. The higher the C3A content of clinker, the more susceptible the concrete is to sulphate corrosion (see Figure 6).

Figure 6: **Sulphate resistance of cement measured on ISO mortar specimen (55 OPC)**
Influence of C3A content on the loss of Young's modulus of elasticity E (determined from ultrasonic pulse velocity measurements)



E28	after 28 days of regular curing = 100%
E180	after 28 days of regular curing and 180 days of exposure to 10% sodium sulphate solution

The rate of sulphate corrosion depends - apart from the C3A content of clinker - on factors other than cement:

- composition of concrete, particularly the water/cement ratio
- age of concrete at the time of the first exposure to sulphates
- type and concentration of sulphate solution
- duration and mode of sulphate exposure

3.2.6 Other properties

The other properties of concrete, such as

- freeze - thaw - resistance
- permeability
- cracking
- shrinkage and creep

are only slightly influenced by the composition of clinker and quality of cement. Other influencing factors, such as air content, w/c-ratio, curing conditions, are decisive.

The cement exerts only an indirect influence on these properties by its effect on the water requirement and rate of hardening.

3.3 Mineral components

(see also paper on blended cements)

The effect of the mineral components on cement performance can be related mainly to their activity. The three main classes of materials in this respect are latent hydraulic (e.g. blast furnace slag), pozzolanic (e.g. fly ash and natural pozzolans) and inert (e.g. limestone).

In case of the active mineral components (latent hydraulic and pozzolanic), the general effects with respect to cement properties are as follows:

- lower water requirement (except for natural pozzolans)
- delay in setting times
- lower heat of hydration
- lower early strength
- higher long term strength
- lower permeability
- improved resistance to sulphate and other chemical attacks
- lower sensitivity for alkali-aggregate reaction

The actual influence on the cement properties will of course still depend on the individual nature of each material. A more detailed comparison on the effects of the main active mineral components blast furnace slag, fly ash and natural pozzolan (at same dosage) is made in Table 4.

Table 4: Effect of main active mineral components on cement properties (general trends)

	Blast furnace slag	Fly ash (class F)	Natural pozzolan
Water requirement	0	↘	↗
Setting time	↗	↗↗	↗↗
Heat of hydration	↘	↘↘	↘↘
Early strength	↘	↘↘	↘↘
Final strength	↗	↗	↗
Sulphate resistance	↗	↗↗	↗↗
Permeability (chloride)	↘	↘↘	↘↘
Alkali-aggregate reactivity	↘	↘↘	↘↘
Shrinkage	0	0	↗

↗ increase
↘ decrease
O neutral effect

The inert mineral components like limestone do exert similar influences as the active materials in terms of water requirement, setting and heat of hydration, but they will not improve the final strength and durability characteristics of the cement.

Other cement properties than the above mentioned are generally not affected to a great extent by the addition of mineral components.

3.4 Gypsum

(see also paper on cement hydration)

The main function of the gypsum in cement is to regulate the cement setting, but the gypsum also influences other cement properties such as grindability, flowability and storage stability, volume stability and strength.

The use of anhydrite instead of gypsum helps to reduce the risk of false setting and to improve the storage stability and flowability of the cement at high grinding temperature (see also chapter 5.6). In case of highly reactive clinkers, proper set retardation may, however, be a problem and blends with gypsum have to be used.

The substitution of natural gypsum by by-product gypsum may sometimes cause problems with setting and strength development due to potential presence of impurities in such type of materials.

3.5 Chemical admixtures

The chemical admixtures, which can be added at the cement mill, are divided into the two following main groups:

- grinding aids having mainly a positive effect on the grinding energy
- performance modifiers influencing significantly the cement quality, in particular water requirement and strength development

The first group of admixtures (typically organic compounds based on alcohol and amines) do as mentioned not really change the engineering properties of cement. The action of the grinding aids is based on the reduction of the adhesive forces between the cement particles. They may, however, facilitate the handling of the cement due to the resulting improvement in flowability.

The performance modifiers are of similar nature as the products used in the concrete mix. Such admixtures are generally based on accelerators and water reducers and thus improve the workability and strength development of the cement.

Needless to say that the use of chemical admixtures is only worthwile if there is a real benefit with regard to the economy or performance of the cement to be produced.

4. OPTIMUM PROPORTIONING OF THE CEMENT COMPONENTS

4.1 General

The proportioning will be discussed here mainly from the point of view of cement performance. The economic aspects, which are of course of primary importance for the proportioning (see chapter 2.5), will not be dealt with, as they greatly depend on the specific circumstances.

For a given cement performance, the proportioning is basically controlled by the quality of the available cement components and the selected fineness of the cement and its components. Further limitations are set by the standards, which specify the permitted contents for the different cement components.

4.2 Clinker and mineral components

Portland cements

In case of the Portland cements, the flexibility in proportioning of clinker and mineral components is obviously limited. According to the European Norm, up to 5% of mineral component can be added to the cement, whereas ASTM does virtually not allow the addition of mineral components besides clinker and gypsum. The focus in the optimisation of the cement properties lies therefore in the determination of the proper gypsum dosage (see chapter 4.3).

Blended cements

The most critical point of the blended cements in terms of cement performance is the decrease in early strength. The dosage of mineral components in general purpose applications, where a similar strength development as for the Portland cement has to be achieved, is therefore limited.

The possible dosages in such applications are the highest for the latent hydraulic mineral components and go gradually down for the pozzolanic and inert materials. Typical proportioning limits for the main mineral components in the cement are:

- blast furnace slag: 30 - 40%
- fly ash (class F): 15 - 30%
- natural pozzolan: 15 - 30%
- limestone. 10 - 20%

For blended cements used in special applications related to low heat evolution and durability, the early strength development is not of primary importance and the dosages of the mineral components can be higher. Some guide values on the proportioning in these applications are given in Table 5. It has, however, to be mentioned that always specific tests should be carried to verify the compliance with the application requirements.

Table 5: Guide values for proportioning of mineral components in cements for special applications

	Blast furnace slag	**Fly ash (class F)**	**Natural pozzolan**
Low heat of hydration	> 50%	> 30%	> 30%
Suphate resistance	> 70%	>30%	> 30%
Low chloride permeability*	> 60%	> 40%	> 40%
Avoidance alkali-aggregate reaction	> 40%	> 25%	> 15%

*provided the w/c-ration in concrete is sufficiently low

The actual proportioning of the mineral components in all applications will obviously also depend on the selected cement fineness and on the permitted contents specified in the respective standards.

4.3 Gypsum

(see also paper on cement hydration)

Portland cements

In Portland cements, the gypsum dosage has to be adjusted to the reactivity of the clinker (i.e. C3A and alkali content) and the cement fineness to ensure proper set retardation. Further adjustments may be necessary depending on the obtained grain size distribution and the grinding temperature in the cement mill.

It is usually assumed that the gypsum dosage for proper set retardation is more or less equivalent to the one required for best strength development and volume stability of the cement. A practical method to find the optimum gypsum content is described in the ASTM standard C 563 ("Standard test method for optimum SO3 in Portland cement"). It is well possible that the SO3 content at the optimum gypsum content would even be above the maximum value given by the standards.

In case that the Portland cement shows false setting tendency and problems with flowability and storage stability, the gypsum content should be lowered or part of the gypsum should be replaced by natural anhydrite. Replacement levels of up to 60% are possible for all type of clinkers without having any problems with set retardation.

Blended cements

In case of blended cements, the situation gets much more complex and there exists no clear procedure on how to adjust the gypsum dosage. Studies at HMC have indeed shown that the optimum gypsum content has to be evaluated for each individual cement type. Nevertheless, the findings indicated that the optimisation of the gypsum content in blended cement can be a very effective means for the improvement of the cement quality.

Special attention in the determination of the optimum gypsum content has to be given to cements, which contain limestone filler. In such cements, it may be possible to reduce the gypsum content, since limestone acts also as a set retarder.

4.4 Chemical admixtures

Grinding aids are added at the cement mill at dosages, which are generally below 500 g/t. The determination of the optimum dosage for a specific grinding aid depends mainly on the cement fineness and the characteristics of the cement mill.

The dosage of the performance modifiers will essentially be determined by the objective for their use. The main purpose of such admixtures is generally to achieve a desired cement performance or to maintain the cement quality at a lower clinker content.

5. CEMENT GRINDING

5.1 General

The cement components have to be ground to fine particles, in order to attain the required cementitious properties. The fineness after grinding is usually characterised by the specific surface area or by the particle size distribution (PSD). The type of cement mill used can have a considerable effect on the PSD.

During the grinding process with the traditional systems (ball mills), only a small portion of the introduced energy is consumed for the comminution of the cement particles. A large quantity of heat is set free and the temperature of ground cement increases appreciably. In the modern grinding systems, less heat is produced, resulting in lower cement temperature during grinding.

Both, the fineness and the temperature of grinding are principal factors in determining the cement properties.

5.2 Description of fineness

5.2.1 Specific surface area

The specific surface area of cement is usually determined by the Blaine method. The Blaine value is calculated from the air permeability of a cement sample compacted under defined conditions. The resistance to air flow of a bed of compacted cement depends on its specific surface. The Blaine specific surface is not identical with the true specific surface of the cement, but it gives a relative value which suffices for practical purposes.

An absolute measurement of the specific surface can be obtained by the nitrogen (or water vapour) absorption method - BET. In this method, the "internal" area is also accessible to the nitrogen molecules and the measured value of the specific surface is therefore considerably higher than that determined by the air permeability method:

Method	**Blaine**	**Nitrogen Absorption (BET)**
Cement A	2'600 cm2/g	7'900 cm2/g
Cement B	4'150 cm2/g	10'000 cm2/g

The Blaine value can sometimes be misleading, especially in the case of outdoor stored clinker, blended cements - consisting of a more easily grindable component - and clinkers containing underburnt material which is easier to grind. The properties of such cements can often be poorer compared to other ground to the same specific surface.

5.2.2 Particle size distribution

Cements of the same specific surface may have different PSD and different properties. Thus, the specific surface is not the only fineness criterion determining the properties of a particular cement composition.

The determination of the PSD can be carried out by the following methods:

- mechanical sieving (residues on sieves of a definite size (e.g. 32, 45 and 60 μμ))
- laser and sedigraph (residues over the whole range of particles sizes)

The mechanical sieving is usually applied in the cement plants. Due to the limitations in sieve sizes, this method does not allow to measure the whole range of particle sizes.

The overall particle size distribution of cement is commonly analysed by means of the theoretical distribution according to Rosin-Rammler-Sperling (RRS), which is described be the following formula:

$$\ln [\ln (100/Rd)] = n [\ln (d) - \ln (d')]$$

being:

Rd = % of particles with diameter greater than d (residue)

d = particle size in μm

d' = characteristic diameter in μm (36.8% of the particles greater than d')

n = slope of RRS straight line

The data obtained in the particle size analysis is accordingly plotted in a so-called RRS-diagram (see Figure 7), having a double logarithmic ordinate (y-axis) and a logarithmic abscissa (x-axis). After linear regression of the particle size distribution, the slope n of the straight line and the characteristic diameter d' (at 36.8% residue) can be calculated.

The slope n and diameter d' are the significant values for the particle size distribution. The first characterises the degree of distribution (wide-narrow), whereas the second one states its location and is an indicator for the overall fineness. High n values results from a narrow PSD and low d' values from a high overall fineness.

Differences in the PSD of cement can also be seen in the relation between the traditionally measured Blaine values and sieve residues. At same sieve residue, the Blaine tends to be lower with higher n values (see also Figure 8).

Figure 7: **Particle size distribution of cement in RRS-diagram**

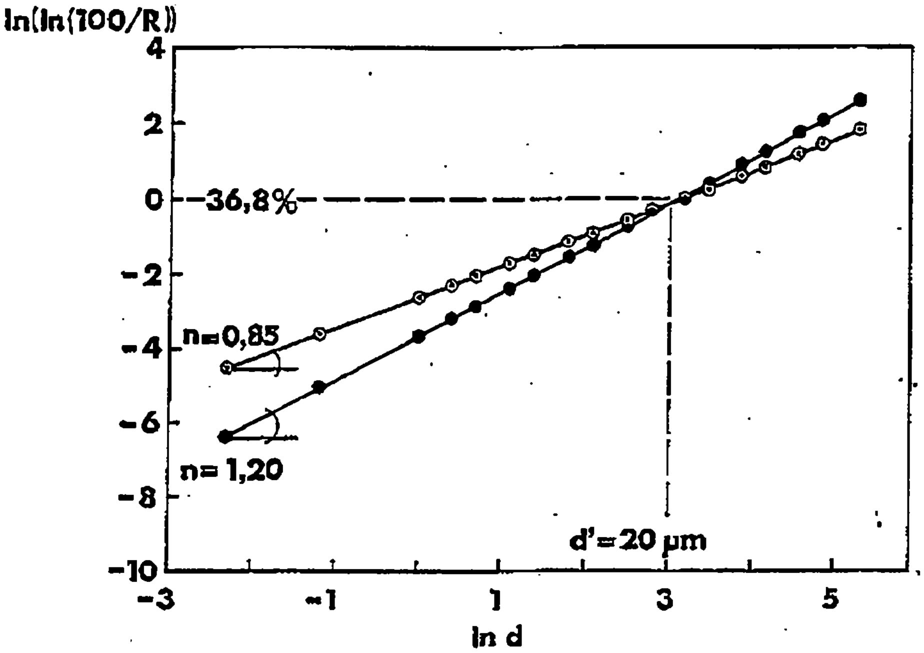
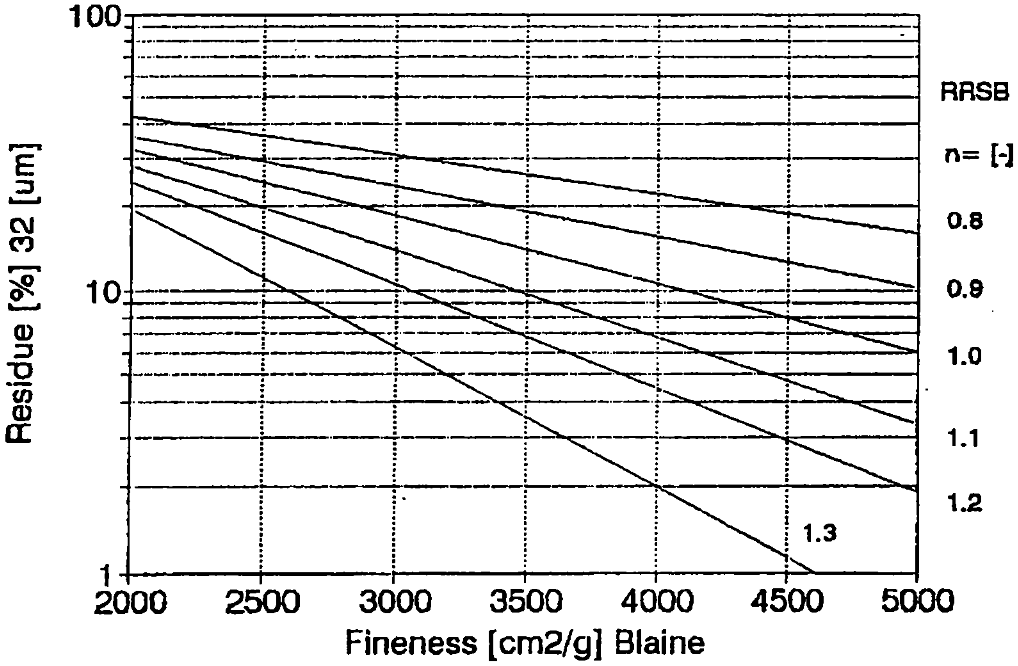


Figure 8: **Correlation between Blaine and residue 32 µm for different n values (data FLS)**



5.3 Particle size distribution in the different grinding systems

The grinding in the modern cement mills goes together with a narrower PSD of the produced cements. Due to the more efficient grinding process, less under- and over-size particles are produced, which obviously leads to a shorter particle range and to higher steepness of the PSD.

The steepness n as expressed by the RRS-distribution ranges from 0.8 for an open circuit ball mill up to 1.2 for the newest grinding systems like vertical mill. Typical n values of cements ground in various industrial mill systems are indicated in Table 6.

The characteristic diameter d' of commercial cements produced in the different grinding systems varies typically between 10 and 30 µm. For identical specific surface, the d' values are lower in the systems which give a narrower PSD, that means that the overall fineness of the cement at same Blaine will be higher. At same d', the Blaine will be lower when the PSD gets narrower.

Table 6: Typical n values for PSD of cements ground in various industrial mill systems

Mill type	Steepness n of RRS-distribution
Ball mill (open circuit)	0.8 - 0.9
Ball mill (closed circuit)	0.9 - 1.0
Ball mill (high efficiency separator)	1.0 - 1.1
Vertical mill, roller press, Horomill	1.1 - 1.2

As mentioned before, the different PSD of the various grinding systems are also reflected in the relationship between Blaine and sieve residues (e.g. on 45 µm), which are the usual fineness measures applied in practice. The corresponding trends observed in the modern grinding systems compared to the traditional ball mills are as follows:

- lower Blaine at same sieve residue or
- lower sieve residue at same Blaine

It is important to mention that, in view of certain quality problems experienced with a too narrow PSD, the actual tendency for the new grinding systems is to adjust the PSD to a somewhat wider distribution.

5.4 Grinding of Portland cements

5.4.1 Influence of Blaine fineness

Since the hydration starts on the surface of the cement particles, it is the specific surface area of Portland cement that largely determines the rate of hydration and thus the setting and hardening rate. To achieve a faster hydration and strength development, rapid-hardening cements are ground finer than ordinary Portland cement. It is common practice to produce cement of various strength classes from one clinker by altering the fineness to which it is ground. The Blaine value of cement varies between 2'500 cm2/g for ordinary Portland cement (type I, ASTM) and 5'000 cm2/g for high early strength cement (type III, ASTM).

The rate of hydration is slowed down by the presence of cement gel and if a large quantity of gel is formed rapidly, because of a large cement surface, the inhibiting action of the gel soon takes place. For this reason, extra fine grinding is efficient only for the early strength up to 7 days. Moreover, the rate at which the strength of concrete increases is substantially lower than that of mortar (see Figure 9).

Considering the energy consumption for grinding, the fine grinding is often not economically feasible. In those cases, where high early strength is not required, fine grinding is of little value (see Figure 10). A large number of concrete applications are unable to exploit the effects of fine grinding.

The relations between the Blaine fineness of cement and concrete properties can be summarised as follows:

1) Increasing the fineness of cement, reduces the amount of bleeding in concrete (see Figure 11).
2) Increasing the fineness of cement above 3000, increases somewhat the water requirement of concrete. Compared to the influences other than cement on the water requirement of concrete, the influence of cement fineness is considerably smaller.
3) The strength of concrete is influenced by the fineness of cement. The early compressive strength increases with an increase in cement fineness. The difference in compressive strength due to the difference in fineness of cement, is considerably smaller at 28 days and at later age (see Figure 9).
4) The fineness of cement influences the drying shrinkage of concrete. When the water content is increased because of fineness, the drying shrinkage is increased.

Figure 9: Effect of cement fineness on strength of mortar and concrete

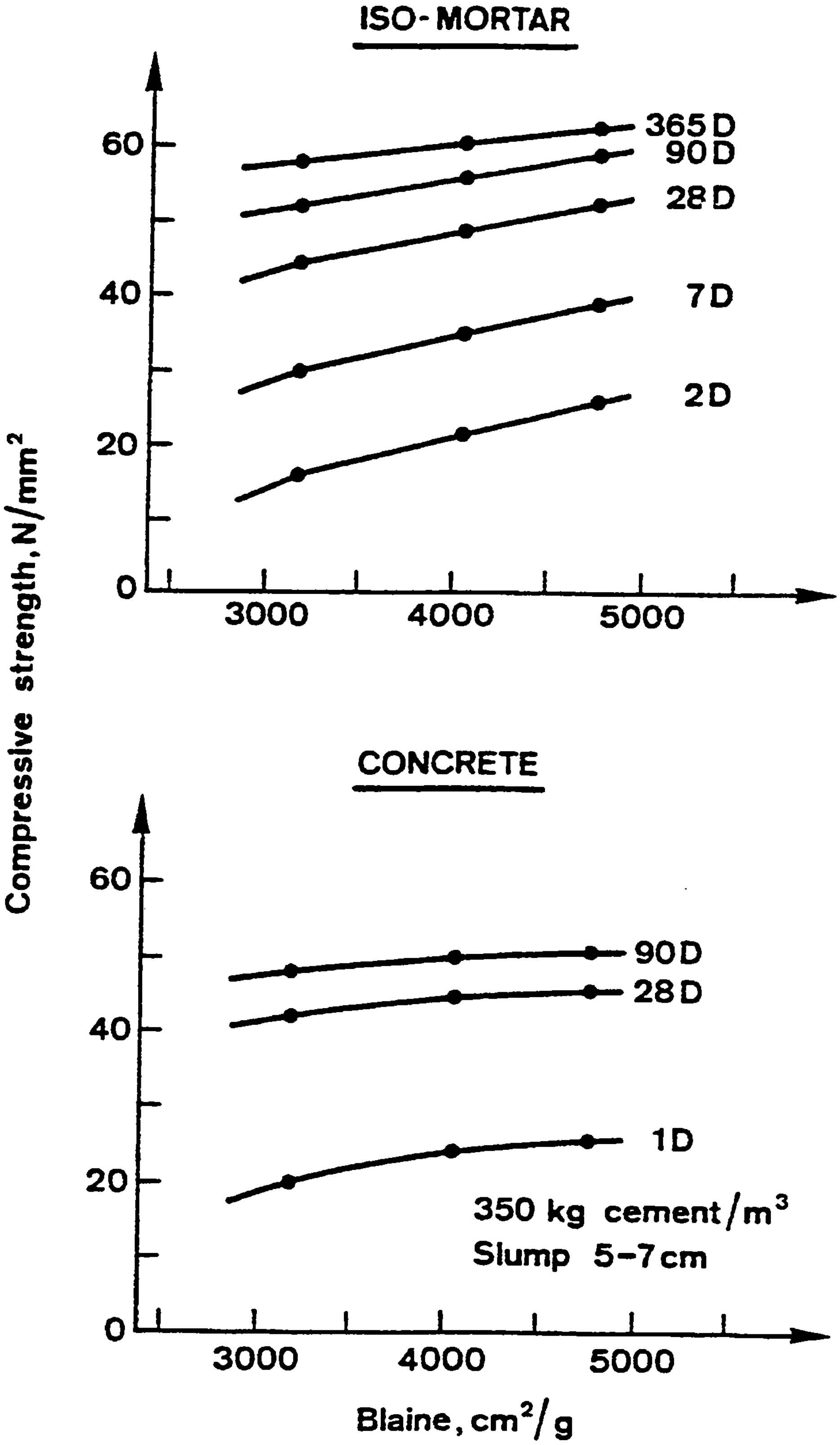


Figure 10: **Relative specific energy consumption and compressive strength development**

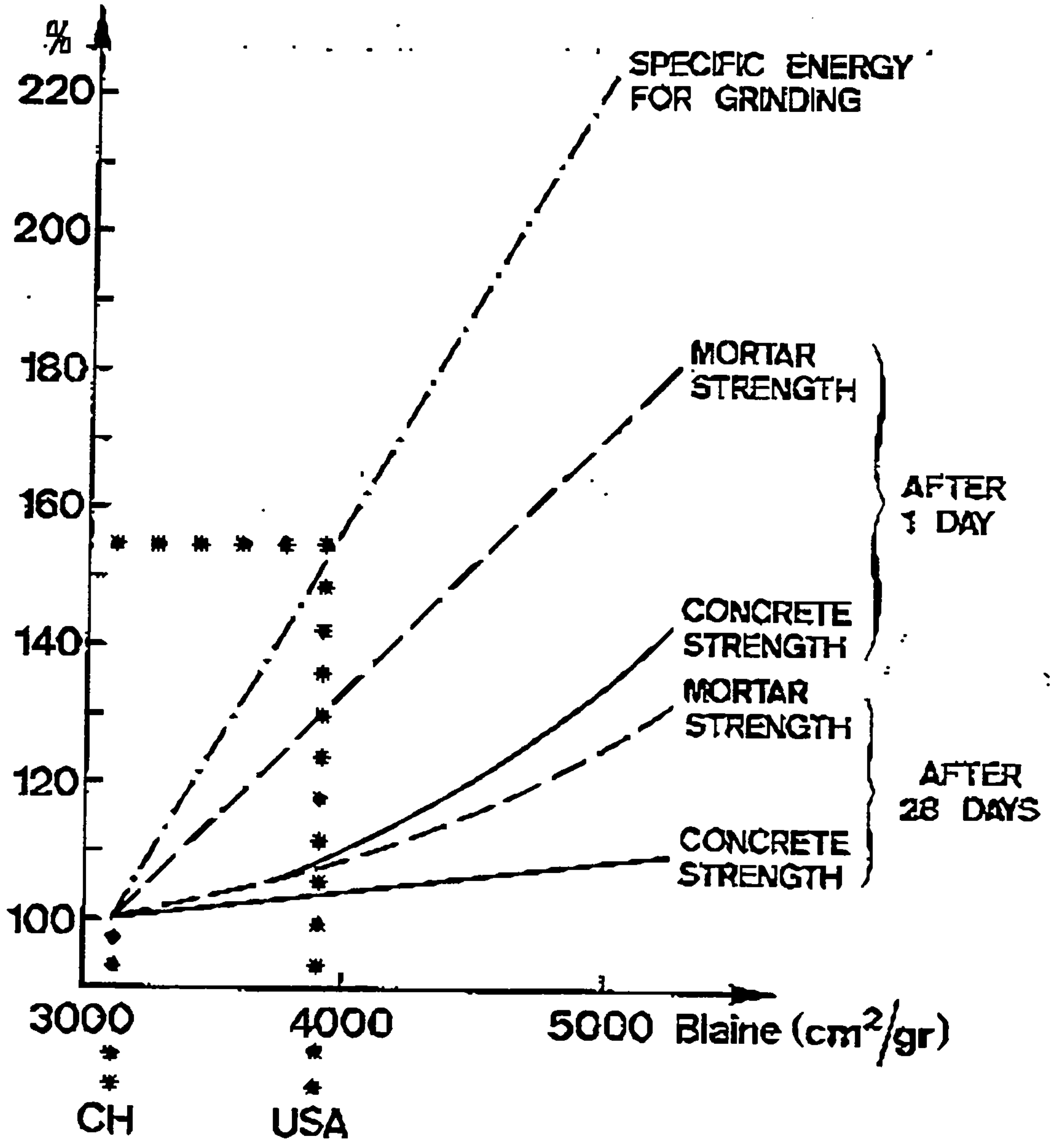
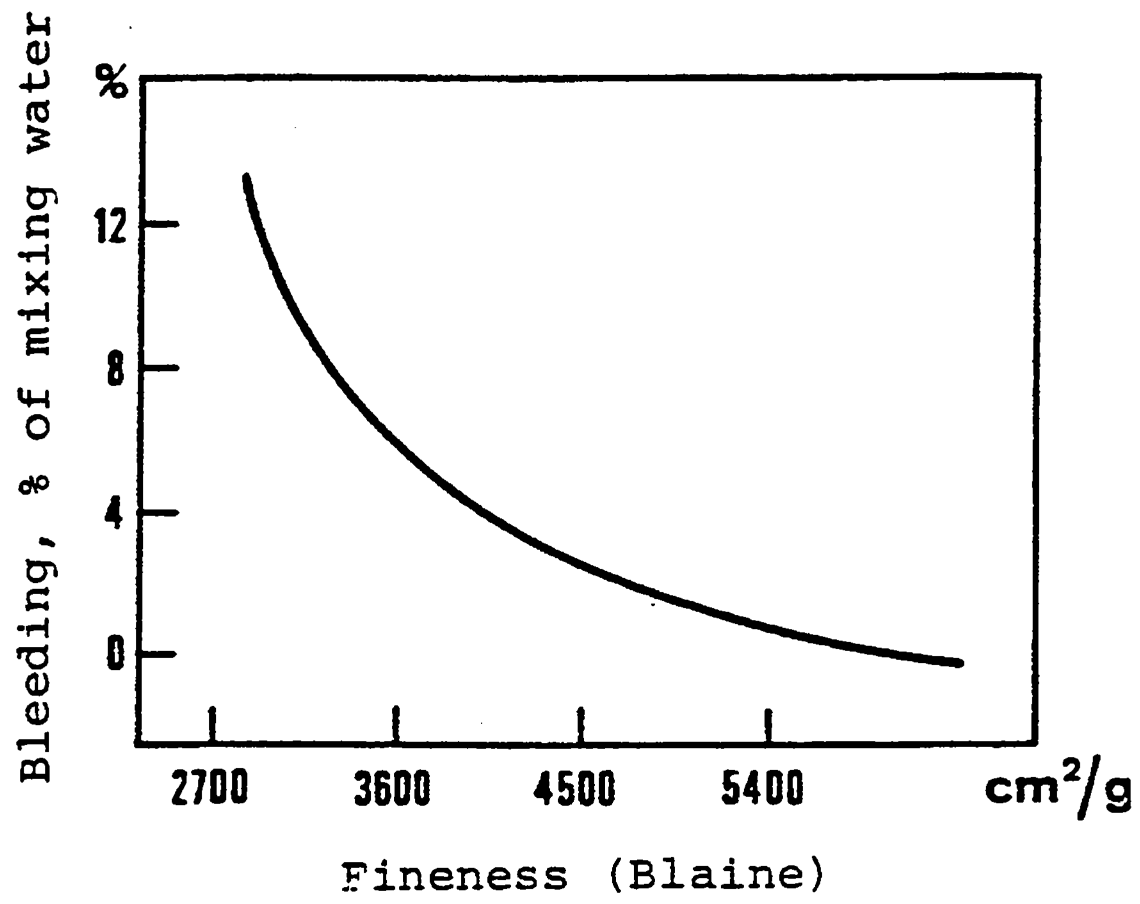


Figure 11: Effect of cement fineness on bleeding of concrete (non air-entrained concrete, w/c-ratio = 0.57)



5.4.2 Influence of particle size distribution

The influence of the fineness on the cement properties can be described more precisely, when taking into account the PSD of the Portland cement. The PSD is of particular importance with respect to workability and strength development.

The workability of Portland cement and concrete may impair when the PSD becomes narrower (at constant specific surface). On one hand, the water requirement for a certain consistency tends to increase and, on the other hand, the faster conversion of aluminate at narrow PSD may lead to early stiffening problems.

The mentioned stiffening problems may especially occur if clinkers of high reactivity (high C3A and alkali content) are ground together with the gypsum at low temperatures (little formation of easily soluble sulphates), as it is the case in the modern grinding systems. With such clinkers, the proper adjustment of the wideness of the PSD and/or of the calcium sulphate carrier is therefore important.

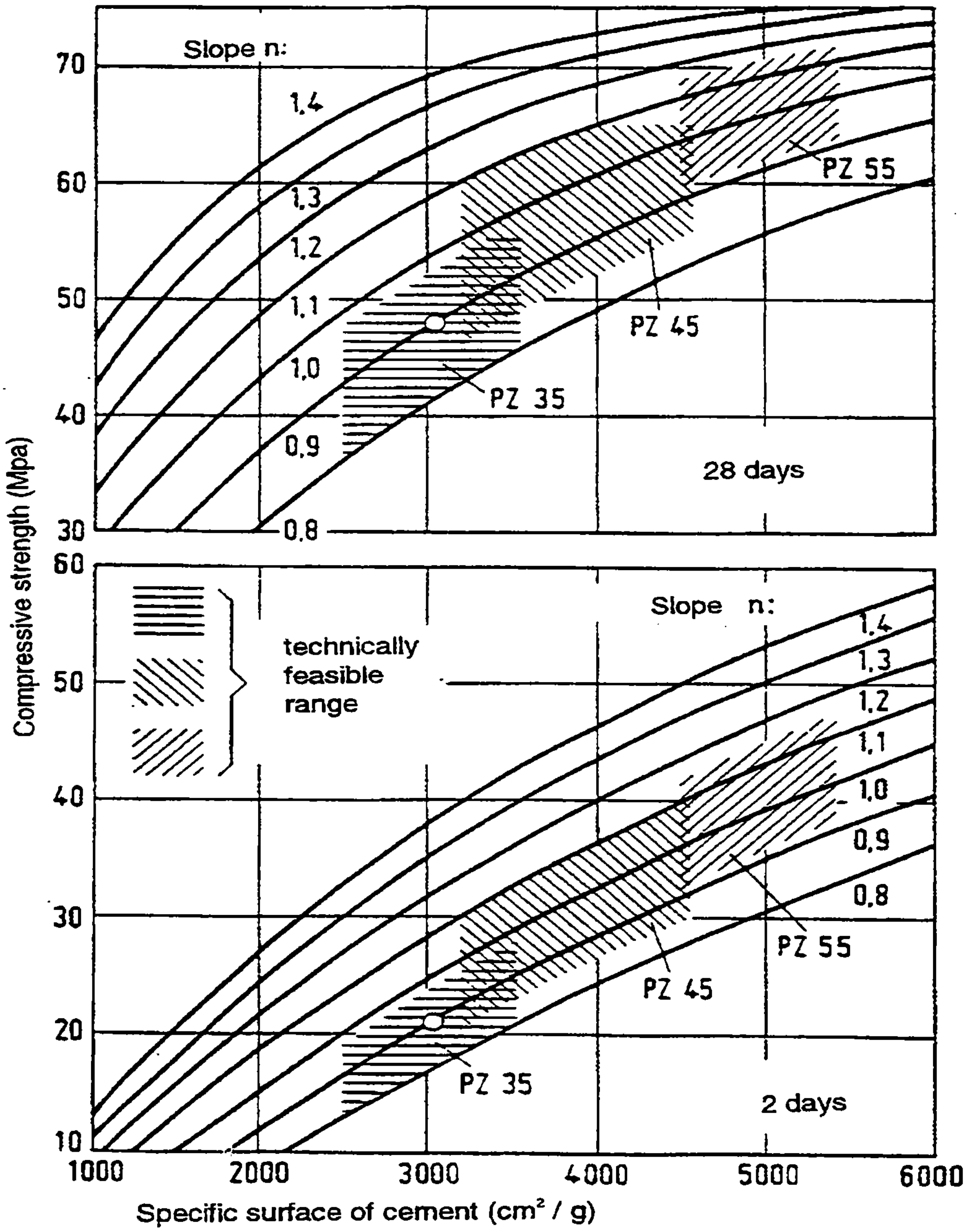
The effect of the PSD of Portland cement on strength development is not always clear. The general trends can be summarised in the following way:

- The most valuable particles for early strength are the ones between 0 - 8 µm. The Blaine value is thus a good indicator in this respect, as it is proportional to the portion in this fraction.

- The 28 day strength is mainly controlled by the amount of particles in the range between 2 - 24 µm, which is proportional to steepness n of the PSD.

The increase in the steepness n at a given Blaine is accordingly an effective means in improving the strength potential at 28 days as illustrated in Figure 12. The positive effects of higher n values are, however, less pronounced on concrete.

Figure 12: **2 day and 28 day compressive strength of Portland cement, as a function of the specific surface area and the slope of the RRS-distribution of the cement**



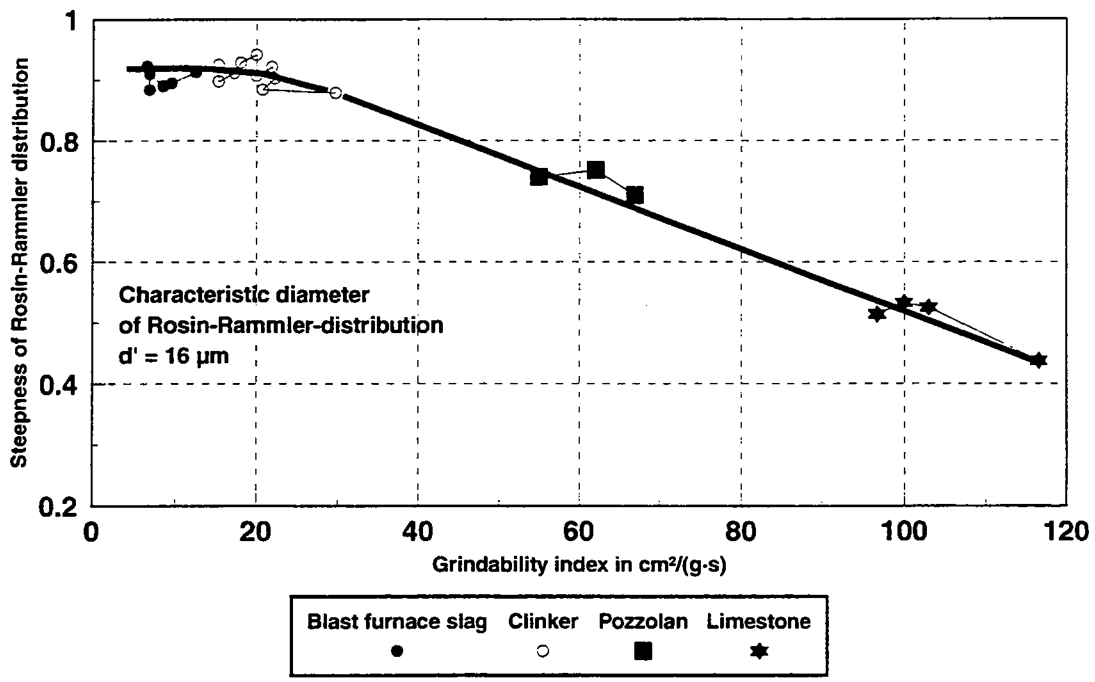
5.5 Grinding of blended cements

5.5.1 General

The properties of blended cements are decisively influenced by the fineness of the cement and its components respectively. Blended cements must generally be ground to a higher overall fineness than Portland cements to maintain a similar strength development.

The grinding behaviour of the different components in blended cements may vary quite significantly as illustrated in Figure 13. At constant fineness, the softer materials like limestone and natural pozzolan yield a wider PSD than the clinker and blast furnace slag. Despite its worse grindability, the grain size distribution of blast furnace slag does, however, not differ too much from the one of clinker. The mentioned differences in grindability are of great significance in the grinding of blended cements.

Figure 13: **Steepness of the RRS-distribution of ground blast furnace slag, clinker, pozzolan and limestone at same characteristic diameter d' in function of the grindability index**



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The question to which fineness the components of blended cements shall be ground to obtain optimum cement properties is often debated. The general concept of HMC is that the hydraulic potential of the clinker should be used as much as possible by grinding it to a sufficiently high fineness. The mineral components may be ground coarser, but latent hydraulic and pozzolanic materials must still have a sufficient fineness to be suitably activated to provide good final strength.

5.5.2 Compound grinding

The compound grinding of clinker, gypsum and mineral component(s) is still the most common practice for the production of blended cements. The combined grinding with mineral components softer than the clinker like limestone will widen the grain size distribution of the resulting blended cement, whereas the mixture of clinker with a harder material like blast furnace slag will give a somewhat steeper PSD than the ground clinker alone. The different PSD can be explained by the fact that for compound grinding, the harder material is enriched in the coarser fraction and the softer material in the finer fractions of the cement.

In compound grinding, the different cement components can accordingly not be ground individually or independently from each other. For a given grinding system, the fineness of the components is pre-determined by their respective grindabilities; it is thus not possible to adjust freely their fineness. The inevitable enrichments of certain components in the fine or coarse fraction of the blended cement are, however, reduced with the modern grinding technologies.

This lack of flexibility in compound grinding may limit the optimisation of the properties of blended cements. With soft mineral components, the clinker will always remain rather coarse, in particular at higher replacement levels, so that its hydraulic potential can not be fully exploited. On the other hand, there might be an overgrinding of the mineral component like in the case of the natural pozzolans leading to an increase in water demand.

In case of slag cement, the clinker will get indeed finer and contribute as desired to the strength development. The slag may, however, not be adequately refined and activated.

5.5.3 Separate grinding

Separate grinding of blended cements gives more flexibility in the design and optimisation of the cement quality than compound grinding, since it permits free choice of the fineness of the cement components. Nevertheless, the opinions on the real benefits of separate grinding are still controversial.

In the following, the experience with separate grinding for the most relevant blended cements containing blast furnace slag, fly ash, natural pozzolan and limestone is discussed.

5.5.3.1 Slag cements

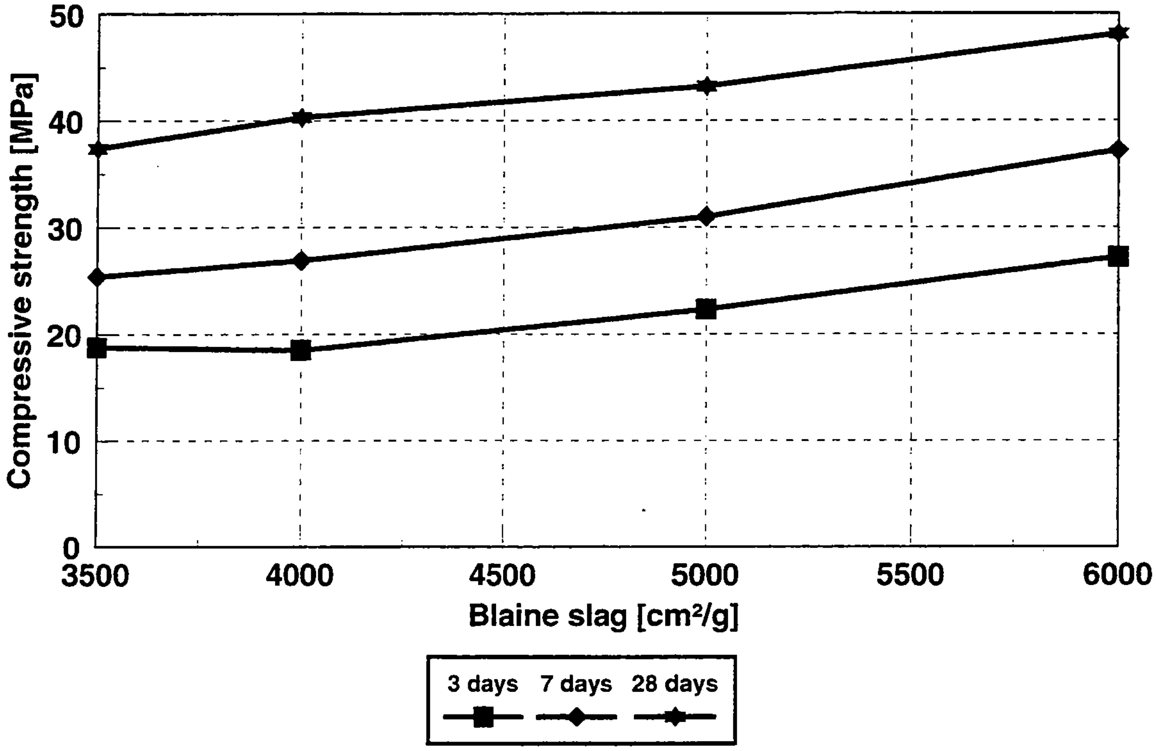
The studies on separate grinding of slag cement revealed that the fineness of the clinker and slag influence the cement quality in the following way:

- the clinker fineness is mainly related to early strength. In cements with low slag content (<30%), the clinker fineness will also have an impact on final strength
- the slag fineness determines mainly the final strength (at very high fineness, also significant contribution to early strength possible). For good workability of the cements, the PSD of the slag should not be too narrow.

In separate grinding, it is thus in principle possible to fine tune the strength curve according to the above relationships. When the grinding energy is kept constant, the observed improvements compared to intergrinding do, however, not seem to be too significant.

An interesting advantage for separate grinding may be in some cases the activation of the slags through very fine grinding. Recent studies have shown that at Blaine finesses higher than 4000, there is a considerable potential to improve the strength development at all ages (see also Figure 14).

Figure 14: Influence of Blaine fineness of slag on compressive strength of ASTM mortar for cement with 40% slag

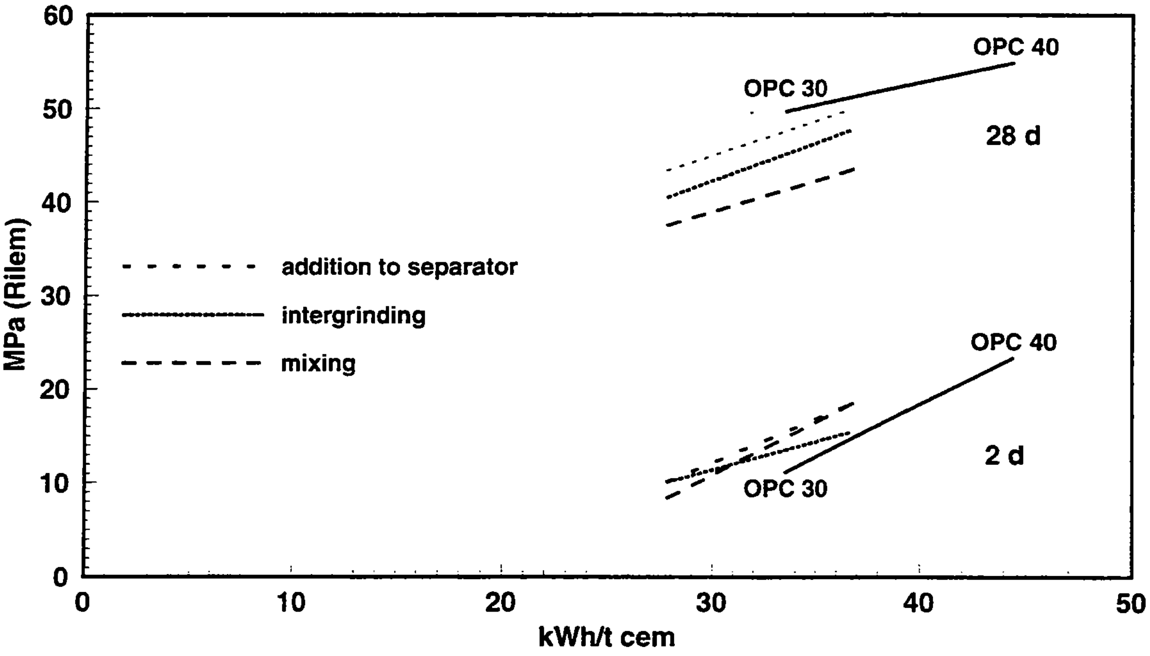


5.5.3.2 Fly ash cements

The separate grinding of fly ash cement as such has hardly been investigated. It appears that at constant grinding energy separate grinding gives certain possibilities to fine tune the final strength development of the fly ash cement.

Presently the most appropriate solution to produce fly ash cements is to add the fly ash to the separator of the grinding system. The example in Figure 15 of a cement containing 16% fly ash demonstrates that in terms of quality and consumption of grinding energy, this seems to be the best solution, also compared to intergrinding.

Figure 15: Influence of treatment undergone by the fly ash on the strength of cement with 16% fly ash



5.5.3.3 Pozzolanic cements

Separate grinding of cements with natural pozzolan gives a somewhat higher early strength and lower final strength than intergrinding at constant energy input. This relationship seems quite logical as in intergrinding the clinker responsible for the early strength remains rather coarse and the pozzolan contributing to the final strength is refined.

The studies on separate grinding of pozzolanic cements carried out at "Holderbank" showed a certain potential to increase the clinker factor at same cement quality, though at the expense of a higher grinding energy. A typical increase might be in the order of 5% as it is illustrated by the comparison of intergrinding and separate grinding for a pozzolanic cement from Mexico in Table 7.

Table 7: Comparison of intergrinding and separate grinding for pozzolanic cement from Mexico

Physical and mechanical properties	Compound grinding (ball mill)	Separate grinding (ball mill and vertical mill)
Cement		
Pozzolan (%)	20	25
Blaine (cm2/g)	4170	4120
n (-)	1.0	x)
R 45 µm (%)	3.3	7.5
Paste ASTM		
Water demand (%)	28.3	27.0
Setting time (min.)		
- initial	160	145
- final	225	175
Mortar ASTM		
w/c-ratio	0.52	0.53
Compressive strength (MPa)		
- at 1 day	11.0	11.6
- at 3 days	20.9	20.7
- at 7 days	27.8	26.0
- at 28 days	35.0	34.8

x) Pozzolan: n = 0.95 R 45 µm = 20.9% Blaine = 2170 cm2/g
Clinker/gypsum: n = 0.95 R 45 µm = 3.1% Blaine = 4300 cm2/g

5.5.3.4 Limestone cements

Studies on separately ground limestone showed that the limestone fineness as such has virtually no influence on the strength development. The PSD of the limestone powder can, however, play a role with regard to the workability characteristics of the limestone cement: a wide distribution is in this respect more favourable than a narrow one.

In combined grinding with clinker, the limestone is automatically ground to the favourable wide PSD. This quite advantageous behaviour in intergrinding, at least at lower limestone dosages (up to 20%) may also explain the fact that separate grinding of limestone cement to improve cement quality has usually not been applied in practice.

5.6 Temperature and moisture conditions

The grinding of cement influences the properties of cement not only through an increase in fineness, but also through the reactions taking place in the cement mill. Depending on the temperature and moisture conditions prevailing in the mill, dehydration and hydration occur which influence the grinding process, flowability, lump formation in silos, setting and hardening of cement.

Due to the heat liberated during the grinding process, the temperature in the traditional ball mills rises to temperatures above 100°C. In the modern grinding systems, the grinding temperatures are significantly lower (down to 50 - 60°C). In a particular mill, the exit temperature of cement can vary in a wide range, in function of the inlet temperature of clinker, cooling conditions and fineness of grinding.

The effect of the grinding temperature on the cement properties is mainly related to the dehydration of gypsum. With increasing temperature, gypsum (CaSO4 2H2O) gets unstable and transforms to hemihydrate and anyhdrite III under the release of water. The dehydration of the gypsum will not only depend on the temperature, but also on the time the gypsum is exposed to this temperature (see Figure 16). Another factor of less importance for gypsum dehydration is the humidity in the mill atmosphere (see Figure 17).

Figure 16: Influence of temperature on the dehydration of gypsum

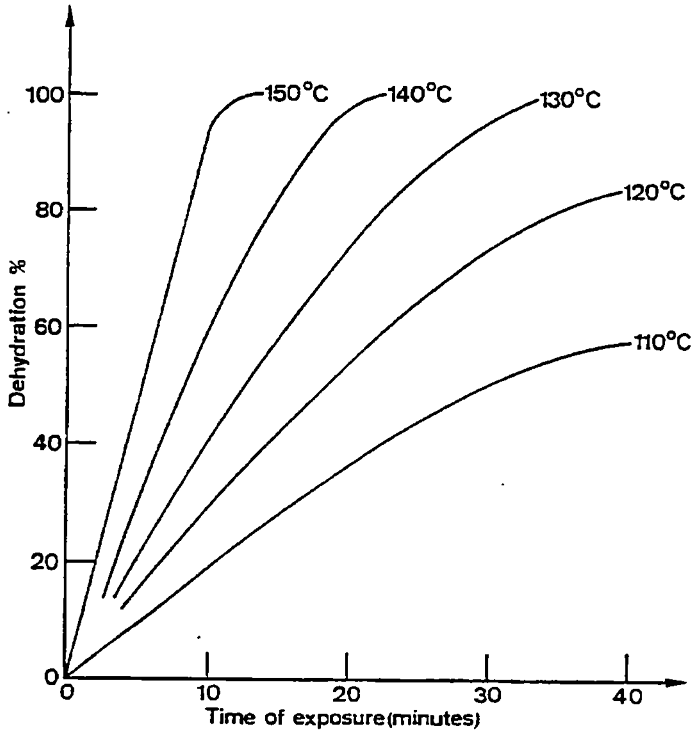
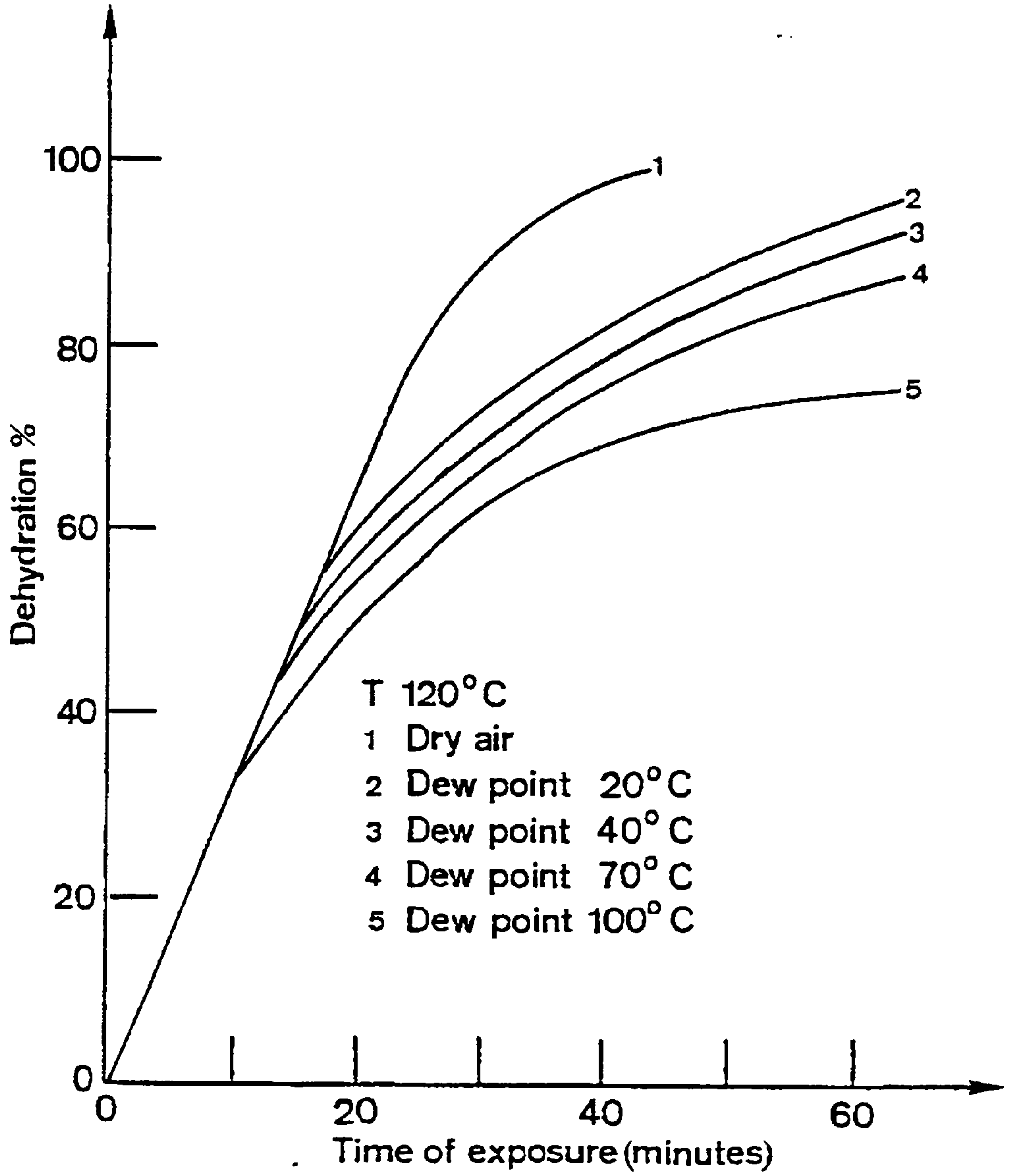


Figure 17: **Influence of humidity on the gypsum dehydration.**



According to the degree of dehydration, the gypsum will exert a different influence on the cement properties (see also paper on cement hydration). If great part of the gypsum is converted to the more easily soluble hemihydrate and anhydrite III, there may be some problems with false setting in case a clinker of low reactivity is used. On the other hand, a too low degree of dehydration may lead to flash setting tendency with reactive clinkers.

The dehydration of the gypsum may also have an impact on the storage stability of the cement. If the cement enters the silo with a high temperature (80 - 90°C), further water can be released form the still not dehydrated gypsum and lead to the hydration of the cement. These hydration reactions can cause lump formation and affect the strength of the cement (see Figures 18 and 19). Clinkers with high C3A and alkali content are particularly subject to hydration reactions during storage.

Figure 18: **Lump formation in a storage sensitive cement after one week storage at various temperatures**

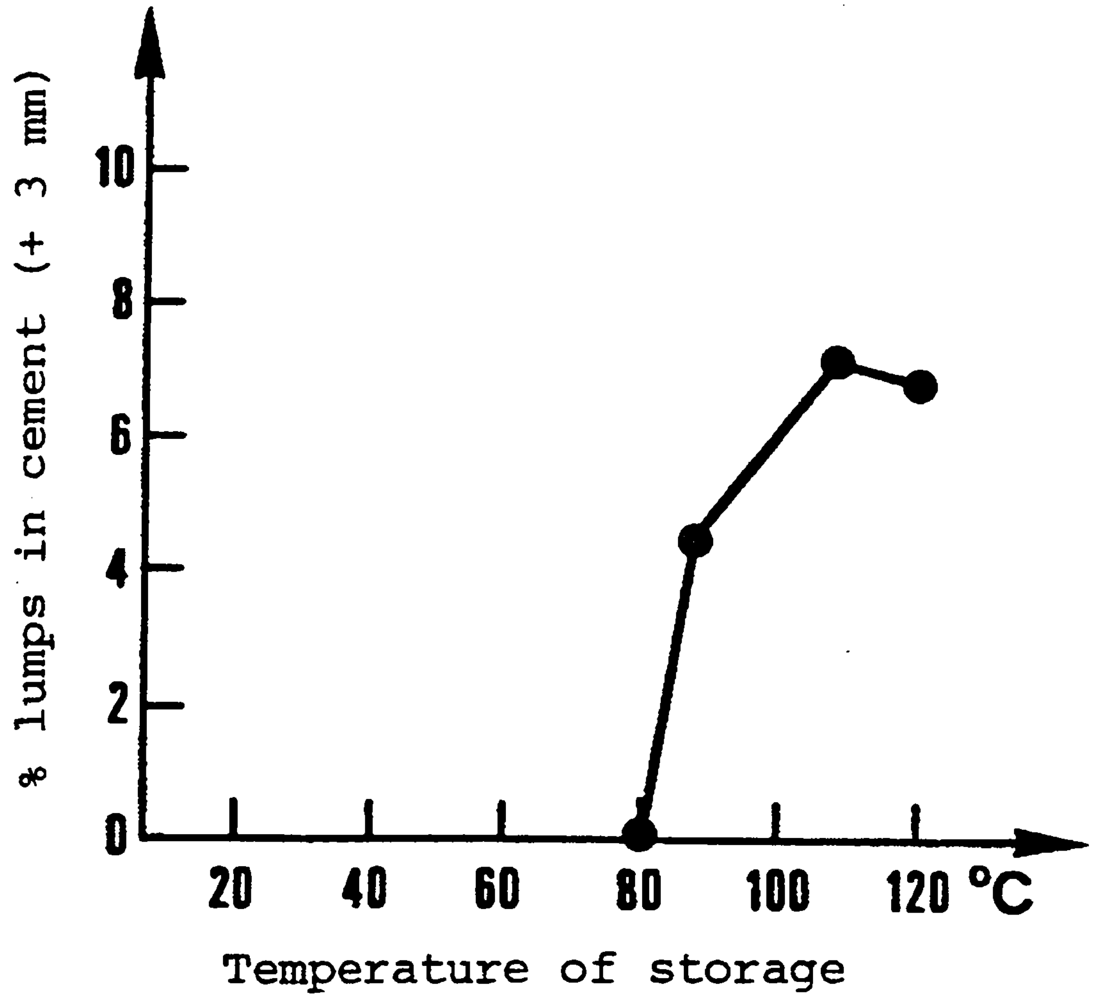
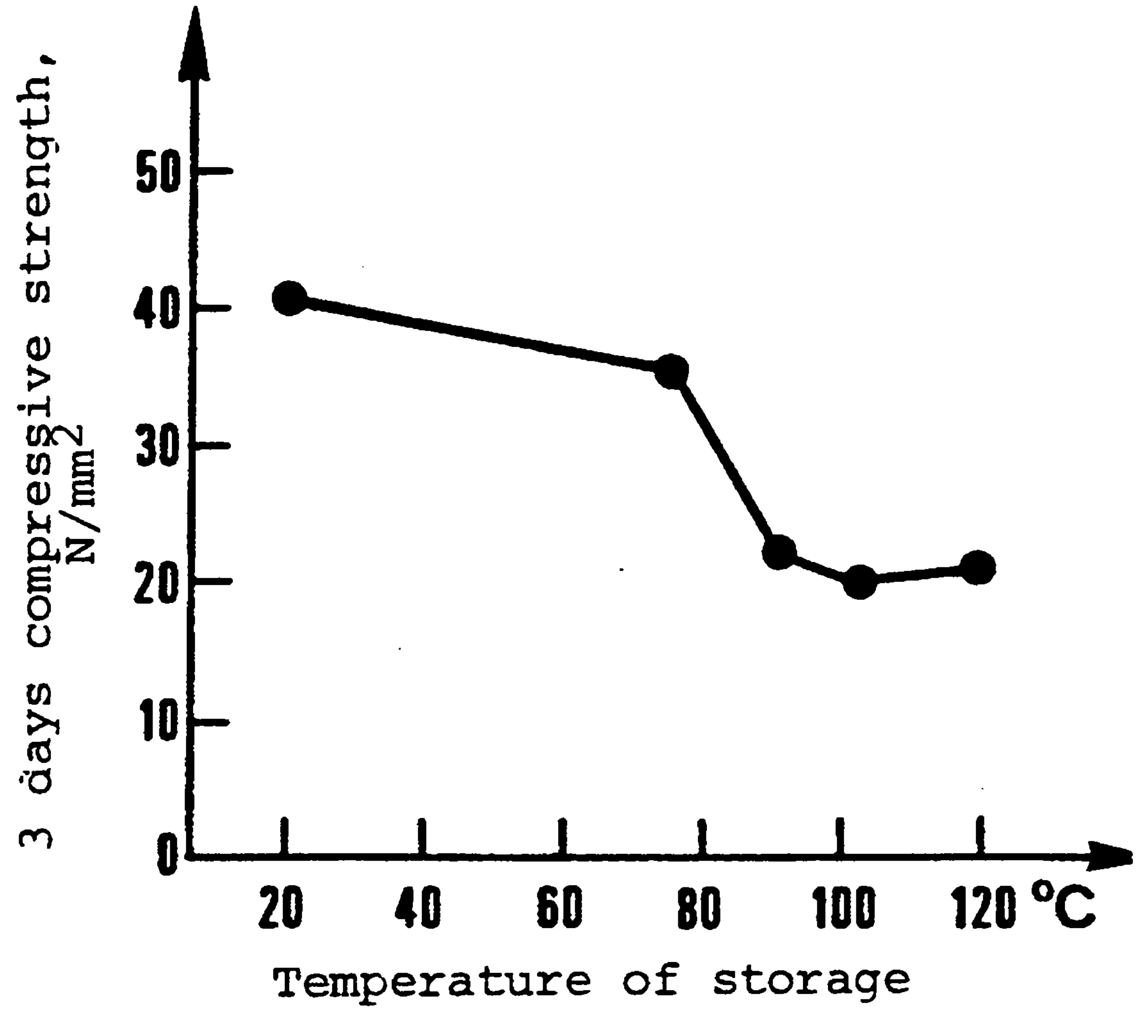


Figure 19: Compressive strength of a storage sensitive cement after one week Storage at various temperatures



Some measures to ensure the storage stability of the cement are:

- low cement temperature in the silo
- short storage time
- reduction of gypsum content in the cement
- substitution of gypsum by natural anhydrite

The storage stability is usually less problematic with the new grinding technologies,where the temperatures of the cement coming from the miss is generaly low. The cement temperatures in ball mills can be lowered by cooling the cement during the grinding process (e.g. water injection) or by installing a cement cooler after the mill. For the cooling by means of water injection, the temperature in the mill should always be kept above 100°C. Otherwise, prehydration of the cement and strength losses may occur.

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